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# THEORY OF OPTICAL ACTIVITY OF CRYSTALS

## I. General Ideas

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### 1. Introduction

The phenomenon of rotation of the plane of polarisation of light traversing an isotropic optically active medium was first explained by Fresnel, near about 1820, by supposing that right and left-circularly polarised light propagate with different velocities in the medium. The electromagnetic theory of light propagation in both isotropic and birefringent optically active media was developed by various authors, in particular by Voigt (1899, 1903) and Drude (1900). This theory is phenomenological in nature and it explains how optical activity varies with direction in a crystal and how it modifies the birefringence exhibited by it. Theories based on the structure of molecules (and crystals) have been proposed by various authors. A review of the theories, particularly in relation to the optical rotation of molecules, has been given by Condon (1937). The theories are, in general, of two types. In the first type, the molecule (or crystal) is treated as a system of coupled oscillators and a study of such a system in the field of the incident light wave leads to the evaluation of the rotatory power. The "coupled-oscillator" theory was first given, simultaneously and independently, by Oseen (1915) and Born (1915). Born's method was applied to the cases of sodium chlorate and bromate by Hermann (1923) and to $\beta$-quartz by Hylleraas (1927). Although these authors found a fairly good agreement with experiment, the calculations are so lengthy and complicated that the application of the method requires a large amount of labour. Kuhn (1929, 1930) gave a simple picture of a coupled oscillator and showed how it led to the presence of optical activity. On this basis, he has also derived the form of a dispersion equation for optical rotation ($\rho$) analogous to the Drude equation for refractive index. The coupled oscillator theory has been formulated in terms of quantum mechanics by Rosenfeld (1928).

The other type of theory, which may be termed the "polarisability theory", attempts to make use of purely optical principles for evaluating the magnitude of the rotation. The atoms, or groups of atoms, of which the

molecule (or crystal) is composed, are polarised in the presence of the field of the light wave. On summing up the induced moments of all the atoms, it would be found that the moment is not in phase with the field of the light wave, which is phenomenologically equivalent to the medium possessing optical activity. Theories of this type have been given by Gray (1916), de Mallemann (1924, 1930) and Boys (1934). Kirkwood (1937) has shown that, by introducing some simplifying assumptions (such as would lead to the additivity law for refraction), the polarisability theory can be derived from the general quantum mechanical formulation of coupled oscillators. Using the simplified result, he also calculated the magnitude of $\rho$ for secondary butyl alcohol and found that it agreed reasonably well with experiment. Kirkwood also showed that earlier authors like de Mallemann and Boys, who made calculations in a practical case, had taken only second and third order terms of his formulation. In this present paper, it is proposed to give a classical picture of the first order terms in the polarisability theory. However, unlike Kirkwood, who applied the theory only to a molecule, we shall develop it for a crystal. In the first part, the general ideas of the theory are presented and are applied to a hypothetical crystal having a spiral structure, which would correspond to an optically active uniaxial crystal. The succeeding parts will contain applications to actual crystals.

The physical basis of the theory is as follows. The different atoms in a molecule, or near neighbours in a crystal, are at finite distances from each other, which, though small, would lead to a variation in the phase of the forced vibration excited by the incident light wave from atom to atom. Consequently, if we determine the influence of the electric moments induced in the neighbouring atoms on any particular atom, there would be an induced electric field which would not be in phase with that of the incident light wave. Under proper conditions, *e.g.*, when the electric vector of the light wave is parallel to a principal axis of the crystal, it would be found that there is a component of the induced electric field at right angles to the incident electric vector, which is 90° out of phase with it. Phenomenologically, this is equivalent to the medium possessing optical activity. As will be seen from the mathematics given below, if one calculates the induced moments in various directions, taking into account the interaction of the neighbouring atoms with the appropriate phases, then it is possible to obtain the magnitude of the optical rotation in all directions of the crystal. The interesting result emerges that, if all the atoms are isotropic, then the optical rotation becomes zero. Anisotropy of the individual atoms (or groups) appears to be essential for optical activity to be present in the first order. However, it may be present as a second or third order effect, *viz.*, the influence of one atom on

another and that again on a third atom, even if all the atoms are isotropic; but obviously the order of magnitude of such effects would be small compared with the first order.

## 2. Electromagnetic Theory of Light-Propagation in Optically Active Crystals

The theory is discussed in detail in several treatises, for instance by Szivessy (1928) and Born (1933). We shall merely quote the results that are of interest for the later sections.

If the co-ordinate axes are taken along the principal axes of the crystal, then the components of the displacement **D** are related to those of the field **E** by the relations

$$D_x = \epsilon_x E_x + i(\mathbf{G} \times \mathbf{E})_x, \text{ etc.} \tag{1}$$

where $\epsilon_x$, $\epsilon_y$, $\epsilon_z$ are the principal dielectric constants and **G** is a vector whose components are given by

$$G_x = g_{11}s_x + g_{12}s_y + g_{13}s_z, \text{ etc.} \tag{2}$$

**s** being a unit vector in the direction of propagation of the light wave. If $n_0'$ and $n_0''$ are the two refractive indices for this direction of propagation in the absence of optical activity (*i.e.*, as calculated from $\epsilon_x$, $\epsilon_y$, $\epsilon_z$), then the two indices in the presence of optical rotation are given by the roots of the equation:

$$(n^2 - n_0'^2)(n^2 - n_0''^2) = G^2, \tag{3}$$

where $G = \mathbf{s}.\mathbf{G}$

$$= g_{11}s_x^2 + g_{22}s_y^2 + g_{33}s_z^2 + (g_{23} + g_{32})s_ys_z + (g_{31} + g_{13})s_zs_x + (g_{12} + g_{21})s_xs_y. \tag{4}$$

The tensor $g_{ij}$ is called the "gyration tensor" and completely describes the optical activity of the crystal.

In the directions of the two optic axes, $n_0' = n_0'' = \bar{n}$ (say). Then,

$$n_l = \bar{n} + G/2\bar{n}, \quad n_r = \bar{n} - G/2\bar{n}$$

and the rotatory power* is

$$\rho = \pi G/\lambda_0 n, \tag{5}$$

where $\lambda_0$ is the wavelength of the light *in vacuo*.

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* For mathematical convenience, and so as to agree with the definitions in later portions, $\rho$ is *positive* for a *left-rotating* crystal and has the same sign as G. This is contrary to the usual definition of rotatory power, which is taken to be positive for right rotation (*cf.* also Szivessy, 1928).

For an arbitrary direction of propagation, the two velocities $n_0'$ and $n_0''$ are given by

$$n_0'^2 = \tfrac{1}{2}\{n_0'^2 + n_0''^2 \mp |\sqrt{(n_0'^2 - n_0''^2)^2 + 4G^2}|\}$$
$$n_0''^2 = \tfrac{1}{2}\{n_0'^2 + n_0''^2 \pm |\sqrt{(n_0'^2 - n_0''^2)^2 + 4G^2}|\},$$

where the upper or lower sign is to be taken according as $n_0' \lesseqgtr n_0''$. Thus the phase difference between the two elliptically polarised waves per unit length, $\Delta$, is given by

$$\Delta^2 = \frac{\pi^2}{\lambda_0^2 n^2}(n_0'^2 - n_0''^2) + \frac{4\pi^2 G^2}{\lambda_0^2 n^2} = \delta^2 + (2\rho)^2, \tag{6}$$

where $\delta$ is the corresponding phase difference when optical activity is absent and $\rho$ is the optical rotation in the direction concerned and is given by the same formula as (5), $n$ now standing for the mean of the two refractive indices.

To make ideas clearer, we may take the case of an optically active cubic crystal, for which $\epsilon_x = \epsilon_y = \epsilon_z = \epsilon$ and $g_{11} = g_{22} = g_{33} = g$ (say) and all other components $g_{ij}$ are zero. For light propagated along Oz, we have

$$\left.\begin{aligned} D_x &= \epsilon E_x - ig\, E_y \\ D_y &= \epsilon E_y + ig\, E_x \end{aligned}\right\} \tag{7}$$

Thus, if the light is polarised with its electric vector along O$x$, then, there is in addition to a displacement $D_x$ also a component $D_y$ at right angles to the electric vector, which is however 90° out of phase with it. Thus, if this perpendicular component is calculated from the structure, then the rotatory power, $\rho$, becomes calculable.

## 3. Principle of the Calculation from Crystal Structure

We shall use throughout Heaviside units for electrical quantities. Consider a crystal having $p$ atoms, designated by 1, 2, . . . . $p$, per unit cell. In some cases, it may be more convenient to take a group of atoms (such as a radical) as a single entity; however, we shall use the term atom in the general discussion to mean both a single atom as well as a group of atoms. The subscript $r$ (1 to $p$) will denote an atom in the unit cell, while the subscript $s$ will denote any general atom, including those in the unit cell. Let $\alpha_{ij}^r$ be the polarisabilities of the different atoms with respect to the chosen co-ordinate system, which has its axes parallel to the principal axes of the optical ellipsoid of the crystal. Let $x_r'$, $y_r'$, $z_r'$ be the co-ordinates of the $r$th atom and let the incident polarised wave (propagated along positive $z$-axis) be represented by $E_x \exp ik(ct - z')$, $(k = 2\pi/\lambda)$, $\lambda$ being the wavelength in the medium. Leaving out the time variable $\exp ikct$, the mean electric field at the atom $r$ is $(E_x + P_x/3) \exp - ikz_r'$, taking into account the Lorenz-

Lorentz field due to the surrounding medium. $P_x$ is the electric moment per unit volume.

We wish now to find the electric field induced at atom $r$ due to its neighbours. For this, choose atom $r$ as origin, so that the co-ordinates of an atom $s$ with respect to this are $x_s = x_s' - x_r'$, etc. The components of the moment induced in atom $s$ by the field of the light wave alone neglecting the interaction of neighbours, are

$$\mu_{xs}' = \alpha_{11}^s(E_x + P_x/3) \exp - ikz_s$$
$$\mu_{ys}' = \alpha_{12}^s(E_x + P_x/3) \exp - ikz_s$$
$$\mu_{zs}' = \alpha_{13}^s(E_x + P_x/3) \exp - ikz_s \qquad (8)$$

These induced moments would produce a field $\mathbf{F}_r$ ($F_{xr}$, $F_{yr}$, $F_{zr}$) at atom $r$. These are given by the formulæ:

$$F_{xr} = \frac{1}{4\pi}\Sigma_s\left(\frac{3x_s^2 - R_s^2}{R_s^5}\mu_{xs}' + \frac{3x_sy_s}{R_s^5}\mu_{ys}' + \frac{3x_sz_s}{R_s^5}\mu_{zs}'\right), \qquad (9)$$

etc., where $R_s$ is the distance between atoms $r$ and $s$ and the summation is to be performed over all atoms $s$ that are significant. It may be noted that we have taken the field at $r$ to be of the same phase as the moment of atom $s$. This is so because $R_s \ll \lambda_s$, the ratio being of the order of 1/1000 and it can be shown that, for an oscillating dipole, the field in its immediate vicinity has the same phase as the oscillations (Hertz, 1889). According to Hertz, the phase retardation $\phi$ at a distance $R_s$ from the dipole is

$$\phi = kR_s - \tan^{-1} kR_s/(1 - k^2R_s^2), \; k = 2\pi/\lambda_0. \qquad (10)$$

This, in fact, leads to a negative $\phi$ (or an advance of phase) for $R_s \sim \lambda_0/8$, $\phi$ becoming zero again at about $R_s = \lambda/4$. In the immediate vicinity of the oscillator, Eq. (10) gives

$$\phi = kR_s[1 - (1 + k^2R_s^2)] = - k^3R_s^3.$$

Thus, the phase change $\phi$ is two orders of magnitude smaller than $kR_s$ (the corresponding change due to the incident wave) and can therefore be neglected in comparison with the latter. Since the phases of the different atoms $s$ would, in general, be different from that of $r$, $F_{xr}$, $F_{yr}$, $F_{zr}$ can be split into the form

$$F_{xr} = F_{xr}' + iF_{xr}'' = (a' + ia'')(E_x + P_x/3), \text{ etc.}$$

Thus, the components of the induced moment in atom $r$, taking the interaction of neighbours also into account, are

$$\mu_{xr} = \alpha_{11}^r(E_x + \frac{P_x}{3} + F_{xr}) + \alpha_{12}^r F_{yr} + \alpha_{13}^r F_{zr}, \text{ etc.} \qquad (11)$$

Summing over the $p$ atoms in the unit cell and dividing by the volume V of the unit cell, we obtain the components of the polarisation **P** as

$$P_x = \frac{1}{V}\sum_p \mu_{xr} = (E_x + P_x/3)(A_x' + iA_x'') \tag{12}$$

and similar expressions for $P_y$ and $P_z$. If these are compared with Eqs. (1), remembering that $\mathbf{D} = \mathbf{E} + \mathbf{P}$, then the values of $\epsilon_x$ and of some of the components of the gyration tensor $g_{ij}$ can be obtained.

Repeating the calculations for the electric vector along Oy and similarly for directions of propagation along Ox and Oy, all the components of the tensors $\epsilon$ and $g$ can be evaluated.

If the calculations are made correctly, the form of equations (1) would be the same as those deduced from the crystal structure—for instance, there would only be an imaginary part in the right-hand side of the expressions for $P_y$ and $P_z$ when the electric vector is parallel to Ox. The exact correspondence of the results from the molecular theory with the phenomenological expressions will be an indication of the correctness of the bases of the theory.

## 4. Calculation of the Rotatory Power along the Optic Axis of a Hypothetical Uniaxial Crystal

In order to illustrate the procedure to be followed in making the calculations, we shall consider a tetragonal crystal having a simple spiral structure. The structure may be described as follows (Fig. 1).

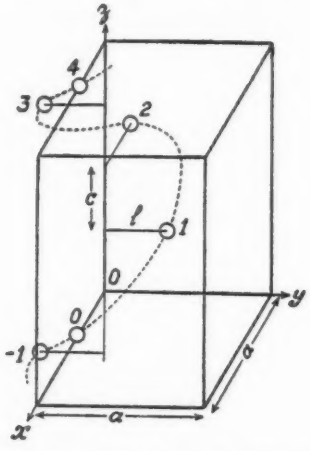


Fig. 1. Unit cell of hypothetical crystal

The unit cell has edges $a$, $a$, $4c$. The $c$-axis is a four-fold screw axis ($4_1$), so that there is a spiral around Oz as axis, the atoms having the co-ordinates $l$, $o$, $o$; $o$, $l$, $c$; $-l$, $o$, $2c$; $o$, $-l$, $3c$. Because of the translational symmetry of the lattice, there will be a similar spiral around each edge of the unit cell, parallel to Oz. The structure belongs to the space-group $D_4^3 - P4_12$, the other enantiomorphous form belonging to the space-group $D_4^7 - P4_32$. The crystal would thus exhibit point-group symmetry $D_4$ and is therefore uniaxial ($\epsilon_x = \epsilon_y \neq \epsilon_z$) and has only two independent components of the gyration tensor $g_{11}$ and $g_{33}$; $g_{22} = g_{11}$ and all other components are zero.

We suppose that $l$ is small compared to $a$, say of the order of $\frac{1}{4}$, so that in calculating the interactions, the effect of atoms in one spiral on those in another may be neglected. Further, we shall only consider the influence of the two nearest neighbours in a particular spiral. The atoms are also supposed to be anisotropic, but for convenience, we take the principal axes of the polarisability ellipsoid to be along Ox, Oy, and Oz. Let the principal polarisabilities of the atom at level O ($z=0$) be $\alpha_1$, $\alpha_2$, $\alpha_3$ along these directions. Then by reason of symmetry, those of atoms at levels 2 and 4 ($z=2c$, $4c$) will be the same, while those of atoms 1 and 3 are $\alpha_2$, $\alpha_1$, $\alpha_3$ respectively.

Consider a wave with electric vector along Ox travelling along Oz. Then the phase of an atom $(x_r, y_r, z_r)$ is $\exp - ikz_r$ and the induced moments, neglecting the interaction of neighbours are

$$\left.\begin{aligned} \mu_{rx}' &= \alpha_1 (E_x + P_x/3) \exp - ikz_r \quad (r \text{ even}) \\ &= \alpha_2 (\quad ,, \quad ) \quad ,, \quad\quad (r \text{ odd}) \end{aligned}\right\} \tag{13}$$

We thus have

$$\left.\begin{aligned} F_{0x} &= \frac{1}{4\pi} \cdot \frac{(3l^2 - R^2)}{R^5} \cdot (\mu_{-1x} + \mu_{1x}) = \frac{1}{4\pi} \cdot \frac{(3l^2 - R^2)}{R^5} \cdot 2\alpha_2 \cos kc\,(E_x + P_x/3) \\ F_{0y} &= \frac{1}{4\pi} \cdot \frac{3l^2}{R^5} \cdot (\mu_{-1x} - \mu_{1x}) = \frac{i}{4\pi} \cdot \frac{3l^2}{R^5} \cdot 2\alpha_2 \sin kc\,(E_x + P_x/3) \end{aligned}\right\} \tag{14}$$

Similarly,

$$\left.\begin{aligned} F_{1x} &= \frac{1}{4\pi} \cdot \frac{(3l^2 - R^2)}{R^5} \cdot 2\alpha_1 \cos kc\,(E_x + P_x/3), \\ F_{1y} &= -\frac{i}{4\pi} \cdot \frac{3l^2}{R^5} \cdot 2\alpha_1 \sin kc\,(E_x + P_x/3), \end{aligned}\right\} \tag{15}$$

$$F_{2x} = F_{0x},\ F_{2y} = F_{0y},\ F_{3x} = F_{1x},\ F_{3y} = F_{1y} \tag{16}$$

Thus,

$$P_x = \frac{2}{V}\left[(a_1 + a_2) + \frac{1}{\pi} \cdot \frac{(3l^2 - R^2)}{R^5} \cdot a_1 a_2 \cos kc\right](E_x + P_x/3) \tag{17}$$

$$P_y = \frac{i}{V} \cdot \frac{1}{\pi} \cdot \frac{3l^2}{R^5}(a_2^2 - a_1^2) \sin kc\,(E_x + P_x/3), \tag{18}$$

where V is the volume of the unit cell.

To take a numerical example, let $a = 6$ Å, $4c = 4$ Å, and let $l$ the radius of the spiral be 1·5 Å. The distance between nearest neighbours in the same spiral is 2·35 Å while the nearest distance between atoms in two different spirals is 4·75 Å, so that we can safely neglect the effect of the latter. Further, suppose $a_1 = 2{\cdot}0$, $a_2 = 2{\cdot}5$, $a_3 = 3{\cdot}0 \times 10^{-23}$. The mean polarisability would roughly correspond to that of an oxygen atom. If we take the light to have a wavelength of 5000 Å *in vacuo*, then $kc \sim 1/1000$, so that we can write $\cos kc = 1$ and $\sin kc = kc$. We then have

$$P_x = 0{\cdot}664\,(E_x + P_x/3); \quad P_y = i\,5{\cdot}94 \times 10^{-5}\,n\,(E_x + P_x/3).$$

From the former, we have $P_x/E_x = 0{\cdot}853$, $n_\omega^2 = 1{\cdot}853$, giving $n_\omega = 1{\cdot}361$. Comparing the ratio of $P_x$ to $P_y$ with the phenomenological equations (1), we have

$$\frac{g_{33}}{n} = \frac{5{\cdot}94 \times 10^{-5}}{0{\cdot}664}(n^2 - 1) = 0{\cdot}763 \times 10^{-4}$$

so that from (5), $\rho = 275°$ per cm.

It is interesting to note that the structure considered above gives a value for the optical rotation which is of the same order as is generally observed. For instance, quartz has almost the same rotation for light of this wavelength.

It may be noticed that $P_x$ is real while $P_y$ is pure imaginary as is required by the electromagnetic theory. The latter requires that, for the same direction of propagation, if the electric vector is along Oy, then $P_y$ must have the same magnitude as $P_x$ formerly, while $P_x$ will have the same value as $P_y$ before, but will be of the opposite sign. This can readily be verified.

## 5. Rotatory Power of the Hypothetical Crystal for Directions at Right Angles to the Optic Axis

Consider light being propagated along positive Ox. If the electric vector is along Oy, the phenomenological equations are

$$D_y = \epsilon_y E_y = n_\omega^2 E_y; \quad D_z = i g_{11} E_y. \tag{19}$$

Calculations similar to those made in the previous section give

$$P_y = \frac{2}{V}\left[(\alpha_1 + \alpha_2) + \frac{1}{\pi} \cdot \frac{(3l^2 - R^2)}{R^5} \cdot \alpha_1\alpha_2 \cos kl\right]\left(E_y + \frac{P_y}{3}\right) \quad (20)$$

$$P_z = -\frac{i}{V} \cdot \frac{1}{\pi} \cdot \frac{3lc}{R^5} \alpha_3 (\alpha_2 - \alpha_1) \sin kl \left(E_y + \frac{P_y}{3}\right). \quad (21)$$

As before, $\cos kl = 1$, $\sin kl = kl$. Comparing (20) and (17) it is seen that the refractive index is the same as before, which is to be expected. Putting in numerical values,

$$P_z = -i \cdot 3 \cdot 96 \times 10^{-5} n (E_y + P_y/3),$$

which leads to a rotatory power $\rho_\perp = -183°$ per cm. Thus the rotatory power at right angles to the optic axis is negative, *i.e.*, in the opposite sense to that along the optic axis, the ratio of the magnitudes being nearly $\frac{2}{3}$. This is not an unreasonable result, since quartz also exhibits a similar behaviour, the rotatory power at right angles to the optic axis being of the opposite sign to that along the optic axis, the ratio of the magnitudes of the two being $\frac{1}{2}$ (Bruhat and Grivet, 1935).

If the electric vector is along Oz, then we obtain

$$P_y = \frac{4}{V}\left[\alpha_3 + \frac{1}{2\pi} \cdot \frac{(3c^2 - R^2)}{R^5} \cdot \alpha_3^2 \cos kl\right]\left(E_z + \frac{P_z}{3}\right) \quad (22)$$

$$P_y = +\frac{i}{V} \cdot \frac{1}{\pi} \cdot \frac{3lc}{R^5} \cdot \alpha_3 (\alpha_2 - \alpha_1) \sin kl \left(E_z + \frac{P_z}{3}\right). \quad (23)$$

The corresponding equations derived from Eq. (1) are

$$D_z = \epsilon_z E_z = n_\epsilon^2 E_z; \quad D_y = -ig_{11} E_z. \quad (24)$$

Comparing (23) and (21), it is seen that the coefficients on the right-hand side are the same, except for a change in sign as is to be expected from the second equations in (19) and (24). But from (22) we now obtain the extraordinary refractive index as $n_\epsilon = 1 \cdot 378$. Thus although the refractive index is different, the rotatory power comes out to be the same, as should be the case if the calculations are correct.

Similarly, for light propagated along the Y-axis, detailed calculations bear out the deductions from Eq. (1), *viz.*,

$$D_x = n_\omega^2 E_x, \; D_z = -ig_{11} E_x; \quad D_z = n_\epsilon^2 E_z, \; D_x = ig_{11} E_z.$$

It is interesting to note that the magnitude of the rotation (both parallel and at right angles to the optic axis) is proportional to $(\alpha_2 - \alpha_1)$, so that they both change sign if $(\alpha_2 - \alpha_1)$ changes sign. Thus, the sense of optical rotation not only depends on the sense of the spiral, but also on the nature of the

anisotropy in the basal plane. In particular, if the atoms are completely isotropic (or at least isotropic in the $xy$-plane), the rotation vanishes. This is, however, an ideal case, for the very existence of a spiral structure would preclude such a possibility. The existence of neighbours arranged in a spiral would itself lead to anisotropy, just as the triangular group $O_3$ of three isotropic oxygen atoms would possess a strong anisotropy because of the arrangement (Bragg, 1924). The calculation of this anisotropy and the consequent rotations however, requires higher order terms.

## 6. Some General Considerations

We have seen how, in the special case considered in the last two sections, the theory leads to results in conformity with the known results regarding optical rotation in a tetragonal crystal. It may be worthwhile to prove generally that the theory leads to the following two fundamental facts of optical activity.

(*a*) The rotation is of the same sense for opposite directions of propagation, and

(*b*) enantiomers will have opposite rotations.

To prove (*a*) we note that in Eqs. (8) and (9) all the quantities are unaltered except that $\exp - ikz_s$ is replaced by $\exp ikz_s$ when the direction of propagation is reversed. Thus, while the real parts of $F_{xr}$, $F_{yr}$, $F_{zr}$ are unchanged, their imaginary parts will have opposite signs. But since the wave vector $s$ in Eqs. (1) and (2) would also change sign, the components of the tensor $g_{ij}$ would have the same sign irrespective of the sense of propagation.

To prove (*b*) we note that enantiomers are related to each other as figures inverted about a centre of inversion. Consequently the co-ordinates $x_s$, $y_s$, $z_s$ of an atom $s$ with respect to an atom $r$ would *all* have opposite signs in the two cases. Thus, in Eq. (9), while terms like $3x_s^2 - R^2$, $3x_sy_s$ will have their signs unchanged, $\mu_s$'s of the two enantiomers would be complex conjugates of each other because of the term $\exp - ikz_s$. Thus, in Eqs. (12) while the real parts are the same for both, the imaginary parts will be of opposite signs. Hence, the refractive indices of the two enantiomers will be the same, but the rotatory powers will be in opposite senses.

Although the theory is not intended to explain the dispersion of optical activity, it is interesting to note that it does explain it fairly accurately. Thus, it is found from the theory that, other conditions being the same, the rotatory power $\rho \propto 1/\lambda_0^2$. This comes from the factor $k\,(=2\pi/\lambda)$ in the expression for $g$ and the factor $1/\lambda$ in the expression for $\rho$ in terms of $g$.

Since the polarisability $\alpha$ would also increase with decrease of wavelength, $\rho$ would vary slightly faster than $1/\lambda^2$. This is in fact the case with a number of substances.


## Summary

The paper contains a classical description of the first order terms in the polarisability theory of optical activity. Optical activity essentially arises because the dipoles induced by the light wave in the medium are not all in the same phase. As a result of their mutual influences, the resultant induced moment will not be in phase with the electric field of the light wave and would lead to a rotation ($\rho$). By comparing the results calculated from the structure with the phenomenological theory of light propagation in the crystal, the magnitude of $\rho$ is obtained. This method has been applied to a hypothetical tetragonal crystal having a spiral structure. It leads to the interesting result that the rotation at right angles to the optic axis is opposite in sign to that along the axis, as in quartz. The theory also predicts that, in general, the rotation will vary faster than $1/\lambda^2$, as is found to be the case with many substances.


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# SYNTHETICAL EXPERIMENTS IN THE CHROMONE GROUP

## Part XXV. A Synthesis of Santal

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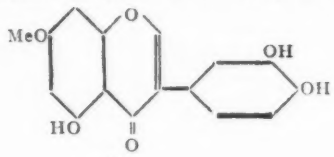
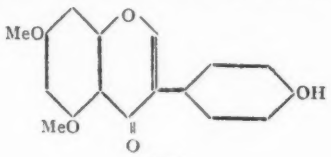
Received December 4, 1950

The dyestuff of the wood of *Pterocarpus santalinus* Linn., variously known as Red Sanderswood, Santalwood and Sandelwood, contains several coloring matters,[1] one of which is santal, first isolated by Weidel.[2] O'Neill and Perkin[3] found that santal, thin plates or flat needles, m.p. 222–23°, was also a constituent of barwood, *Baphia nitida*, Lodd. Santal, $C_{16}H_{12}O_6$, contained one methoxyl group, and demethylation with hydriodic acid gave santol, $C_{15}H_{10}O_6$, crystallizing in colorless needles, m.p. 270–73°. Robertson, Suckling and Whalley[4] have recently investigated the constitution of santal, which they isolated from commercial camwood (a variety of barwood), and also from sandelwood. Santal gave a triacetate and a trimethyl ether; the latter yielded 2-hydroxy-4:6-dimethoxybenzoic acid by ozonolysis, and 2-hydroxy-4:6-dimethoxyphenyl 3:4-dimethoxybenzyl ketone, together with formic acid, by hydrolysis with alcoholic caustic potash. The constitution of santal, therefore, was 5:3′:4′-trihydroxy-7-methoxyisoflavone (I). Robertson, *et al.* also synthesized the trimethyl and triethyl




(I)



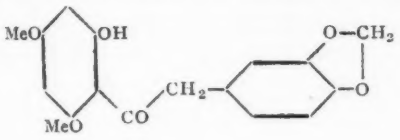

(II)

ethers of santal, following the ethyl formate method for isoflavone synthesis.[5] Demethylation of santal gave norsantal (O'Neill and Perkin's santol), which was apparently identical with orobol occurring as the glucoside, oroboside, in *Orobus tuberosus*.[6] We have now confirmed the constitution of santal by synthesis.

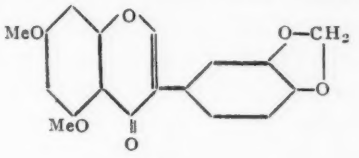
As an extension of our work on prunetin,[7] the synthesis of santal was undertaken, since 4′-hydroxy-5:7-dimethoxyisoflavone (II) appeared to be a suitable intermediate. In the synthesis of prunetin, the preferential demethylation of the 5-methoxyl group has been shown to be feasible in an

isoflavone, and the problem in the conversion of (II) to santal was to introduce a hydroxyl group in the 3′-position. The acetate of (II) was submitted to the Fries reaction with the object of carrying out a Dakin oxidation subsequently on the 3′-acetyl derivative of (II), but under the conditions tried so far, deacetylation with the regeneration of (II) or the formation of prunetin took place. The introduction of an aldehyde group in the 3′-position by the hexamine reaction was not practicable. The oxidation of (II) with benzoyl peroxide in chloroform[8] led to a mixture of products from which the 5-methyl ether of santal was not isolable, although the use of a solvent in which (II) is more soluble and modified conditions might yield the desired substance. The 3′-benzeneazo derivative of (II) offers another route to santal analogous to the method we have used for the synthesis of 5:6-dihydroxyflavone; but (II) was oxidized by diazonium salts under the usual alkaline conditions and remained unaffected under other conditions.

Anhydrous aluminium bromide has been employed by Pfeiffer for demethylation,[9] and by Mosettig and Burger[10] for the scission of a methylenedioxy group (*e.g.*, in piperonal), both the reactions taking place at low temperature (about 10°). An aluminium bromide complex of the mono- or dihydric phenol is formed, and is then hydrolysed by dilute hydrochloric acid. Preliminary experiments indicated that aluminium bromide in nitrobenzene at room temperature (about 30°) converted 5:7-dimethoxyisoflavone smoothly into 5-hydroxy-7-methoxy-isoflavone,[7] and also converted pseudobaptigenin (7-hydroxy-3′:4′-methylenedioxyisoflavone)[11] into 7:3′:4′-trihydroxyisoflavone. A method for the synthesis of santal thus became




(III)




(IV)

available. 2:4:6-Trihydroxyphenyl 3:4-methylenedioxybenzyl ketone, prepared by the Hoesch reaction between phloroglucinol and 3:4-methylenedioxyphenylacetonitrile, was methylated to the dimethyl ether (III) by means of dimethyl sulphate and potassium carbonate in acetone. The ethyl orthoformate reaction[12] proved to be inapplicable to (III), and since the analogue without the methylenedioxy group readily yields 5:7-dimethoxyisoflavone by the action of ethyl orthoformate, the specific effect of this group is being investigated further. By the older ethyl formate-sodium method[5] (III) gave a good yield of the isoflavone (IV). When (IV) was

treated with aluminium bromide (3 mols.) in nitrobenzene solution at room temperature for two hours and the product worked up, 5:3′:4′-trihydroxy-7-methoxyisoflavone (I), agreeing in all its properties with santal, was obtained.

Demethylenation with aluminium bromide has interesting possibilities for syntheses in the flavone and isoflavone series; thus the action of aluminium bromide on 3:5:7-trimethoxy-3′:4′-methylenedioxyflavone[13] should readily yield rhamnetin.

## Experimental

*2:4:6-Trihydroxyphenyl 3:4-methylenedioxybenzyl ketone*

A slow stream of dry hydrogen chloride was passed for four hours through an ice-cooled solution containing dry phloroglucinol (14 g.), 3:4-methylenedioxyphenylacetonitrile (18 g.), fused zinc chloride (5 g.) and anhydrous ether (120 c.c.). The reaction mixture was kept in the refrigerator for 48 hours. The ether was decanted off and the solid ketimine hydrochloride washed with ether, treated with 600 c.c. water, refluxed for two hours, and cooled. The product (21 g.) was collected and crystallized from dilute alcohol; the colorless rods had m.p. 202° (Found: C, 62·4; H, 4·0. $C_{15}H_{12}O_6$ requires C, 62·5; H, 4·2%). An alcoholic solution of the substance gives with ferric chloride a wine-red colour which becomes brown with excess of the reagent.

*2-Hydroxy-4:6-dimethoxyphenyl 3:4-methylenedioxybenzyl ketone (III)*

2:4:6-Trihydroxyphenyl 3:4-methylenedioxybenzyl ketone (20 g.) in boiling acetone (250 c.c.) was treated with dimethyl sulphate (13·5 c.c.; 2 mols.) and freshly ignited potassium carbonate (35 g.) during 14 hours. Acetone was recovered and water added to the residue. The solid was filtered and washed with water (16 g.). It crystallized from alcohol in elongated plates, m.p. 97° (Found: C, 64·1; H, 4·9. $C_{17}H_{16}O_6$ requires C, 64·5; H, 5·1%). The alcoholic solution gives a reddish brown colour with ferric chloride.

*5:7-Dimethoxy-3′:4′-methylenedioxyisoflavone (IV)*

The ketone (III) (10 g.), in freshly distilled ethyl formate (300 c.c.) was gradually added to finely powdered sodium (10 g.) at room temperature. A vigorous reaction took place and the mixture turned reddish brown. The reaction mixture was kept at room temperature, poured into ice and hydrochloric acid, and allowed to stand when a pale brown solid (9 g.) separated. It crystallized from alcohol in plates, m.p. 135–40°. This sample on sublimation at 250–60°/30 mm. gave a substance melting at 156° (Found: C, 66·1; H, 4·2. $C_{18}H_{14}O_6$ requires C, 66·3; H, 4·3%). Cyclization

of the ketone (III) to the isoflavone (IV) was indicated by the absence of ferric chloride reaction and the insolubility in aqueous caustic soda.

5:3':4'-*Trihydroxy-7-methoxyisoflavone* (*I* ; *santal*)

The compound (IV) (1·89 g.) in dry nitrobenzene (40 c.c.) was added to an ice-cooled solution of freshly distilled aluminium bromide (4·65 g.; 3 mols.) in nitrobenzene (40 c.c.). After keeping at room temperature (30°) for two hours, the mixture was diluted with ether and shaken with ice and hydrochloric acid. The clear ether-nitrobenzene layer was separated from the aqueous hydrochloric acid layer, and from a slight resinous precipitate, washed free from acid, and extracted four times with 10 c.c. portions of 2·5% caustic soda solution. The alkaline extract was treated with ether to remove traces of emulsified nitrobenzene, separated from the ether layer and acidified. A pale brown solid (1·0 g.) separated. After three crystallizations from alcohol, the cream-coloured plates were dried in vacuum over calcium chloride at room temperature and had m.p. 223° (Found: C, 60·0; H, 4·6. $C_{16}H_{12}O_6$, $H_2O$ requires C, 60·4; H, 4·4%). Robertson, *et al.*, describe the compound as yellow plates and quote m.p. 223° for the monohydrate, unchanged on sublimation at 190–200°/0·0005 mm. The m.p. of our synthetic sample remained undepressed when mixed with a sample of santal kindly supplied by Dr. Whalley. An alcoholic solution of the substance gives a violet-red color with a drop of alcoholic ferric chloride, and the color becomes reddish brown with excess of the reagent. Robertson, *et al.*, observed a brownish red ferric chloride reaction. Addition of a drop of 10% aqueous caustic soda to a suspension of the compound in water produces a colorless solution changing rapidly to red and then gradually to green on standing. Addition of excess 10% aqueous caustic soda gives a colorless solution changing immediately to red and rapidly to green. We have performed the color reactions of natural santal side by side with our synthetic sample and we find that their reactions are identical.

*Santal triacetate*

Santal (0·2 g.), acetic anhydride (5 c.c.) and pyridine (0·5 c.c.) were refluxed for four hours and then poured over crushed ice. The pale brown solid (0·2 g.) was collected and crystallized from ethanol. The product melted at about 135°, and the alcoholic solution gave a pale brown color with ferric chloride indicating the presence of a trace of partially acetylated material. Recrystallization from absolute methanol gave colorless needles, which were free from ferric reaction and melted at 170°, alone or when mixed with santal triacetate.

SUMMARY

Santal, a constituent of sandelwood (*Pterocarpus santalinus* Linn.) and of barwood (*Baphia nitida* Lodd.), has been shown by Robertson, Suckling and Whalley to be 5 : 3′ : 4′-trihydroxy-7-methoxyisoflavone. A synthesis of santal is now described. 5 : 7-Dimethoxy-3′ : 4′-methylenedioxyisoflavone (IV) has been prepared by the action of ethyl formate and sodium on 2-hydroxy-4 : 6-dimethoxyphenyl 3 : 4-methylenedioxybenzyl ketone at room temperature. By the action of aluminium bromide on (IV) in nitrobenzene under specified conditions, demethylenation and preferential demethylation in the 5-position were effected, and the product agreed in all its properties with santal.

ACKNOWLEDGMENT

We are greatly indebted to Dr. W. B. Whalley of the University of Liverpool for samples of santal and its triacetate and to Mr. T. S. Gore, B.Sc. (TECH.), for carrying out the microanalyses recorded in the paper.

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# A NOTE ON 4:5:6-TRIMETHOXY-COUMARAN-3-ONE

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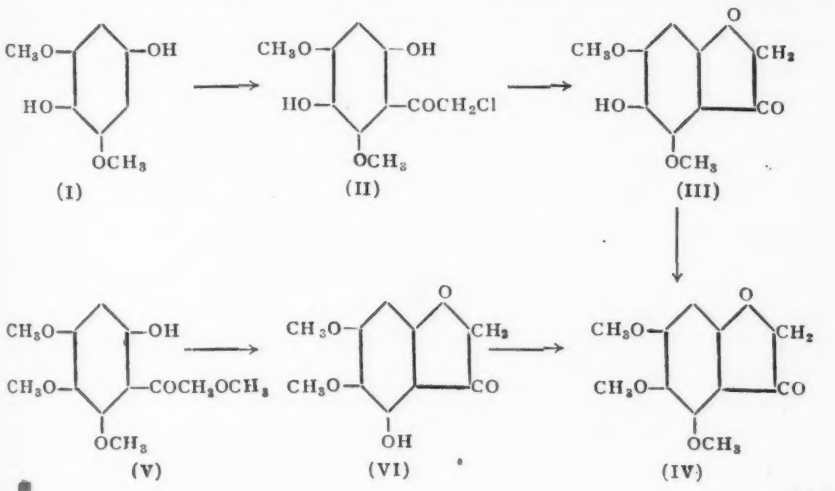
In connection with a method for distinguishing between flavones and flavonols, the preparation of a number of coumaranones and their derivatives was earlier investigated.[1] As a continuation, the preparation and properties of 4:5:6-trimethoxy-coumaranone (IV) is here described. The starting material is 2:6-dimethoxy quinol (I) which is unreactive in the Hoesch condensation for the preparation of ketones. But it reacts smoothly with chloracetyl chloride in the presence of anhydrous aluminium chloride in the cold and the product is found to be 2:5-dihydroxy-4:6-dimethoxy-ω-chloroacetophenone (II); no demethylation occurs during this condensation. Under the same conditions the quinol does not enter into reaction with acetyl chloride. Treatment with sodium acetate in hot alcoholic solution converts (II) into 4:6-dimethoxy-5-hydroxy-coumaranone (III) which yields 4:5:6-trimethoxy-coumaranone (IV) by methylation. This sample is found to be identical with the product obtained by the degradation of quercetagetol-tetramethyl ether (V)[2] in the following manner. When this ω-methoxy ketone is heated with 40% aqueous hydrogen bromide,



it yields a coumaranone giving ferric chloride reaction. Obviously partial demethylation takes place in the course of this reaction in the 4-position (VI). It is therefore directly methylated whereby the trimethoxy compound (IV) is obtained.

## Experimental

2 : 5-*Dihydroxy*-4 : 6-*dimethoxy*-ω-*chloroacetophenone* (*II*) :

Anhydrous aluminium chloride (16 g.) was added in small quantities at a time to dry ether (50 c.c.), cooled in ice, followed by 2 : 6-dimethoxy-1 : 4-dihydroxy benzene (I) (7 g.). Chloracetyl chloride (4 g.) was then added gradually in drops and the mixture allowed to stand overnight. Ice-cold water (50 c.c.) and concentrated hydrochloric acid (50 c.c.) were added in small quantities alternately, all the while allowing the ether to evaporate. The reaction mixture was then heated on a boiling water-bath for one hour, cooled and the separated solid filtered off. It crystallised from alcohol as light yellow elongated rectangular rods melting at 154°. Yield 4 g. (Found: C, 48·4; H, 4·8; $OCH_3$, 25·5; Cl, 14·0; $C_{10}H_{11}O_5Cl$ requires C, 48·7; H, 4·5; $OCH_3$, 25·2; Cl, 14·4%). With alcoholic ferric chloride it gave a brown colour and was soluble in aqueous alkali. It produced an irritating sensation when it came in contact with the skin.

4 : 6-*Dimethoxy*-5-*hydroxy*-*coumaran*-3-*one* (*III*)

The above compound (II) (4 g.) was dissolved in a small quantity of alcohol and an aqueous solution of sodium acetate (10 g. in 100 c.c.) was added to it. The mixture was boiled for 15 minutes when a grey solid separated out. It was cooled and filtered. It crystallised from methyl alcohol as light grey hexagonal prisms melting at 88–89°. Yield 2 g. (Found: C, 57·2; H, 5·0; $OCH_3$, 29·1; $C_{10}H_{10}O_5$ requires C, 57·2; H, 4·8; $OCH_3$, 29·5%). With alcoholic ferric chloride it did not give any colour but it was soluble in aqueous alkali.

4 : 5 : 6-*Trimethoxy*-*coumaran*-3-*one* (*IV*) :

(i) The above hydroxy compound (III) (1 g.) was dissolved in dry acetone (25 c.c.) and treated with anhydrous potassium carbonate (5 g.) and dimethyl sulphate (3·0 c.c.). The mixture was refluxed for three hours and the potassium salts were filtered off. On concentrating the filtrate, the trimethyl ether separated out. It crystallised from alcohol as pale yellow prisms melting at 108–09°. Yield 0·4 g. (Found: C, 58·7; H, 5·6; $C_{11}H_{12}O_5$ requires C, 58·9; H, 5·4%.) With alcoholic ferric chloride it did not give any colour and was insoluble in aqueous alkali.

(ii) Quercetagetol-tetramethyl ether (V) (2·0 g.) was treated with aqueous hydrobromic acid (40%, 10 c.c.) and the mixture heated on a boiling water-bath for three hours. Water was added and the solid that separated out was extracted with ether. Removal of ether gave a solid which even after a crystallisation from methyl alcohol did not have a sharp melting point, gave colour with alcoholic ferric chloride and was almost completely soluble in aqueous alkali. It therefore seemed to consist largely of 4-hydroxy-5: 6-dimethoxy-coumaranone arising out of partial demethylation in the course of the reaction. It was methylated completely using excess of dimethyl sulphate and anhydrous potassium carbonate in dry acetone medium according to the procedure described above. The trimethoxy-coumaranone (IV) thus obtained crystallised from alcohol as pale yellow prisms melting at 108–09°. The mixed melting point with the sample obtained in (i) was not depressed. Yield 0·1 g.

SUMMARY

4: 5: 6-Trimethoxy-coumaranone is obtained from quercetagetol-tetramethyl ether by treatment with hydrobromic acid and methylation of the product. It is conveniently synthesised from 2: 6-dimethoxy-quinol which undergoes Friedel and Craft's reaction with chloracetyl chloride satisfactorily.

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# RAMAN SPECTRUM OF LITHIUM AMMONIUM TARTRATE MONOHYDRATE

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## 1. Introduction

Padmanabhan (1948, 1950) has made a detailed investigation of the Raman spectra of a series of six crystalline tartrates which included Rochelle salt and sodium ammonium tartrate. Crystalline lithium ammonium tartrate whose electrical properties have been extensively studied, is found to be transparent to the ultraviolet and hence its Raman spectrum has been investigated using the $\lambda$ 2537 mercury resonance radiation as exciter. The results obtained are described in this paper.

The specimen of lithium ammonium tartrate used for the present study was in the form of a thin rectangular plate of dimensions $16 \times 12 \times 3$ mm. Light from the mercury arc was incident on the broad face of the crystal and the scattered light was taken through the edge. Using a slit width of 0·035 mm. and a Hilger medium quartz spectrograph, an exposure of thirty-six hours was found to be necessary to get a picture with reasonable intensity. Another spectrogram was taken with a different orientation of the crystal in which the light was incident on the broad face while the scattered light was taken through the edge which is perpendicular to the former one. The frequency shifts of the lines were accurately estimated by comparison with a standard iron arc spectrum which was partially superposed over the Raman spectrum.

## 2. Results and Discussion

An enlarged photograph of the Raman spectrum of lithium ammonium tartrate and its microphotometric record are reproduced in Fig. 1. The mercury lines are indicated in the figure by the symbol $\lambda$. The recorded spectrum exhibits thirty-seven Raman lines. In Table I are listed the frequency shifts along with those of ammonium tartrate observed by Padmanabhan (1950). The figures given in brackets represent visual estimates of the relative intensities of the lines. Almost all the lines appear quite sharp in the spectrum.

TABLE I

*Frequency Shifts in Wavenumbers*

| Lithium Ammonium tartrate | Ammonium tartrate | Lithium Ammonium tartrate | Ammonium tartrate |
|---|---|---|---|
| 50 (2) | | 1212 (4) | 1215 |
| 67 (2) | 64 | 1240 (2) | 1265 |
| 82 (7) | 78 | 1318 (10) | 1313 |
| 104 (8) | 95 | 1346 (6) | 1334 |
| 126 (5) | 115 | | 1364 |
| 149 (7) | 136 | 1378 (1) | 1388 |
| 170 (2) | 168 | 1402 (3) | 1407 |
| 192 (1) | 193 | 1421 (15) | 1445 |
| | 215 | 1460 (3) | 1468 |
| 245 (1) | 245 | | 1493 |
| | 294 | | 1579 |
| | 355 | 1635 (1) | 1607 |
| 469 | | 2836 (2) | 2781 |
| 522 (1) | 537 | | |
| | 703 | 2878 (7) | |
| 808 (7) | 805 | 2921 (1) | 2917 |
| 842 (2) | 840 | 2944 (8) | 2945 |
| 892 (2) | 901 | 2978 (6) | 2968 |
| 915 (3) | 920 | 3005 (6) | |
| 975 (2) | | 3029 (2) | 3002 |
| 988 (2) | 988 | | 3160 |
| 1070 (8) | 1073 | 3413 (7) | 3430 |
| 1109 (2) | 1103 | | 3378 |
| 1157 (2) | 1128 | | |
| | 1192 | | |

Like Rochelle salt, lithium ammonium tartrate also belongs to the orthorhombic class of crystals. Further details regarding its crystal structure are not available.

*Lattice spectrum.*—There is a close correspondence between the lattice spectrum of lithium ammonium tartrate and that of ammonium tartrate. As is to be expected, because of the lower mass of the lithium ion, the frequency shifts in the case of the former are slightly higher than the corresponding ones of the latter. Of the eight lattice lines with frequency shifts 50, 67, 82, 104, 126, 149, 170 and 192, the more intense ones, namely 82, 104, 126 and 149 are almost equally spaced. The other four lines are rather feeble, but they are easily discernible in the microphotometric record.

*The tartrate spectrum.*—The twenty-seven Raman lines with frequency shifts lying in the range from 245 to 3005 cm.$^{-1}$ are due to the internal oscillations of the tartrate ion. The most important feature of the spectrum which is not found in the Raman spectra of other crystalline tartrates so far studied is the appearance of a group of six lines with frequency shifts 2836, 2878, 2921, 2944, 2978 and 3005 cm.$^{-1}$ due to the C–H oscillations. It is

interesting to note that the spectra of aqueous solutions of tartrates and of crystalline potassium tartrate exhibit only one Raman line characteristic of the C–H oscillation. When the atomic mass of the cation is lowered, the line due to the C–H oscillation gets split up giving rise to two lines in the case of sodium and ammonium tartrates and their mixed salts and six in the case of lithium ammonium tartrate. The presence of six lines in the latter case may be due to the greater influence of the lighter lithium ion on the C–H oscillation.

The frequency shifts of the Raman lines due to carboxyl, C–OH and C–C group oscillations show a general correspondence with those of other tartrates. In the spectrum of lithium ammonium tartrate the lines at 245, 469 and 522 cm.$^{-1}$ arising from the deformation oscillations of the C–C chain are very weak as compared with those appearing in the spectrum of Rochelle salt.

*Oscillations due to the water molecule.*—Lithium ammonium tartrate contains one molecule of water of crystallisation. Unlike in the case of other tartrates, its spectrum exhibits only a single sharp line at 3413 cm.$^{-1}$ This frequency shift agrees well with that due to the symmetric O–H oscillation in water.

*Spectrum of the $NH_4$ ion.*—It is interesting to note that the characteristic frequencies of the $NH_4$ ion are very much suppressed in the spectrum of this double salt. In fact the only Raman line which can be attributed with certainty as due to the internal oscillations of the $NH_4$ ion is the one at 3029 cm.$^{-1}$ which appears very weak in the spectrum. Similar behaviour is exhibited by sodium ammonium tartrate.

### 3. Effect of Crystal Orientation

Two different spectrograms of the crystal were taken with the light incident on the broad face (16 × 12 mm.) of the crystal and the scattered light taken normally from the

(1) Perpendicular to the edge 16 × 3 mm. and

(2) Perpendicular to the edge 12 × 3 mm. respectively.

Since the structure of the crystal is not known, the orientations of the crystal with respect to the actual crystallographic axes could not be specified. In the two spectra the Raman lines with frequency shifts 50, 88, 104, 522, 988, 1109, 1378, 1421, 2944 and 2978 cm.$^{-1}$ are found to undergo marked variation in intensity. A correspondence is noticeable between these Raman lines and those in the case of Rochelle salt and sodium tartrate (Padmanabhan,

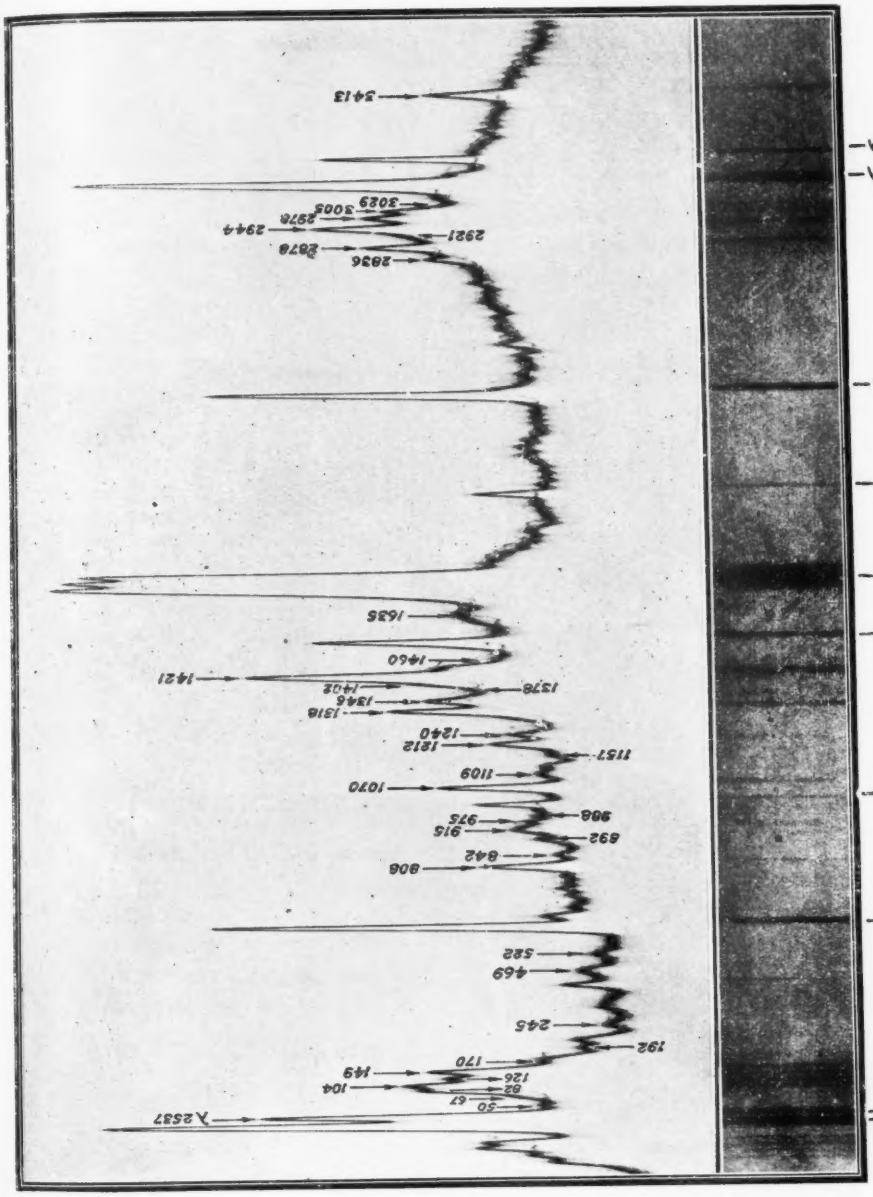


FIG. 1. The Raman spectrum of lithium ammonium tartrate monohydrate with λ 2537 excitation

1949) which also showed similar variation in intensity. These lines can be tentatively assigned as due to symmetric oscillations.

I am extremely thankful to Professor R. S. Krishnan for his suggestions and encouragement in the present work. The specimen of lithium ammonium tartrate used in the investigation was the one presented by Dr. W. P. Mason of the Bell Telephone Laboratories to whom the author's thanks are due.

## Summary

Using $\lambda$ 2537 resonance radiation as exciter, the Raman spectrum of a single crystal of lithium ammonium tartrate has been recorded for the first time. The spectrum exhibits thirty-seven Raman lines. The observed frequency shifts are compared with those of other tartrates. The frequencies due to the $NH_4$ ion are seen to be very much suppressed in the spectrum of this crystal.

A few of the Raman lines show marked variations in intensity with orientation of the crystal.

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# RAMAN SPECTRUM OF POTASSIUM DI-HYDROGEN PHOSPHATE

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## 1. Introduction

The Raman spectra of ammonium and potassium di-hydrogen phosphates have been investigated by Jean Chapelle (1949) and Landsberg and Baryshanskaya (1949). In the case of $KH_2PO_4$, Chapelle, using the visible rediations of the mercury arc, identified 7 frequency shifts of which the two low frequency ones have been attributed to the rotational oscillations of the $H_2PO_4$ group around the two-fold axis. Comparing his results with those obtained by the author (Narayanan, 1948) in the case of $NH_4H_2PO_4$, it became clear that the lattice spectrum of $KH_2PO_4$ as recorded by Chapelle was incomplete. The author had occasion to study the Raman spectrum of $KH_2PO_4$ after that of $NH_4H_2PO_4$ using the resonance radiation of mercury as exciter. However, before the author could publish his results, Chapelle's paper on the subject appeared. Nevertheless, the author's investigation has brought to light the existence of some detail not observed by Chapelle. It was therefore considered worth while to put the same on record.

## 2. Experimental Results

A fine transparent specimen of $KH_2PO_4$ (2 cm. × 2 cm. × 1 cm.) with the faces 100, 010, 101 and 011 fully developed was used to record the Raman spectrum excited by $\lambda$ 2537. Fig. 1 (*a*) is a reproduction of the microphotometer record of the spectrogram obtained when the incident light was along *a* and the scattered light was along the optic or *c* axis, while Fig. 1 (*b*) corresponds to the case in which the scattered light was taken along the *a* axis with the incident light along *b* axis. The spectrum consists of 15 lines some of which are broad and diffuse; the frequency shifts of these are 50, 98, 114, 153, 185, 358, 370, 393, 467, 528, 570, 913, 1080, 2500 and 2700 cm.$^{-1}$ of which those at 98, 114, 358, 393, 459, 531 and 911 cm.$^{-1}$ above have been reported by Chapelle in his published paper. In a private communication, he informed the author about his having recorded the bands at 2500 and 2700 cm.$^{-1}$ also. The lines at 114, 153, 370, 467, 2500 and 2700 are of different

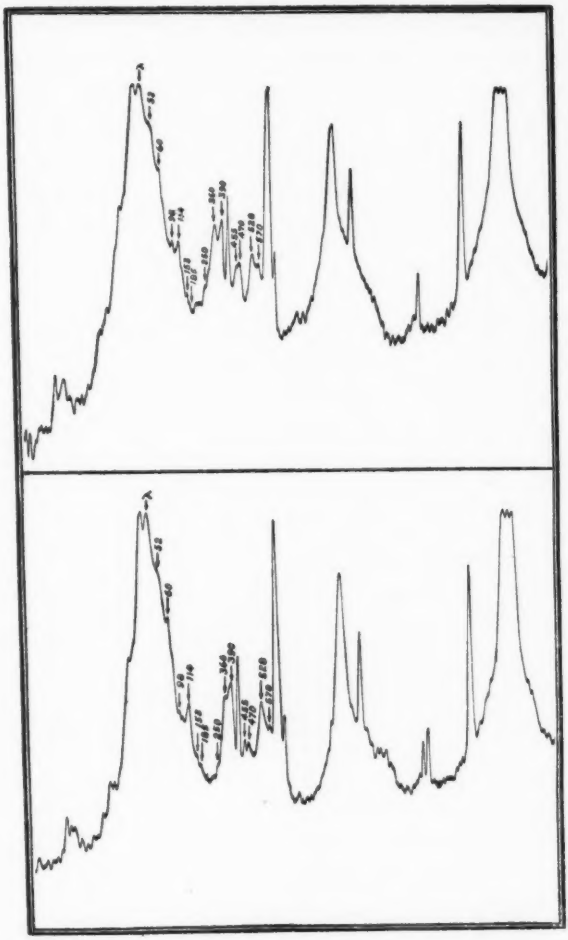

FIG. 1 (*a*)

FIG. 1 (*b*)

FIG. 1. Microphotometer curve of the Raman Spectrum of $KH_2PO_4$

intensity in the two orientations studied, all of them except 114 and 153 being absent when the optic axis is perpendicular to the directions of the incidence and scattering. The line 114 cm.$^{-1}$ is, however, nearly absent when the optic axis is along the direction of scattering.

## 3. DISCUSSION

Potassium di-hydrogen phosphate is isomorphous with $NH_4H_2PO_4$ and belongs to the space group $V_d^{12}$. The structure is based on two

interpenetrating body centred tetragonal lattices. The interatomic distances suggest that the $H_2PO_4$ ion which is so stable in solution (C. S. Venkateswaran, 1938) is still present as a unit in the solid state (J. C. Slater, 1940). In order to write down the character table for the unit cell, the co-ordinates of the hydrogen atoms are taken as $\frac{1}{4}\,u\,\frac{1}{8}$; $u\,\frac{3}{4}\,\frac{7}{8}$; $\frac{3}{4}\,\bar{u}\,\frac{1}{8}$; $\bar{u}\,\frac{1}{4}\,\frac{7}{8}$; etc.

TABLE I

| $V_d$ | E | $2S_4^2$ | $C_2''$ | $2C_2$ | $2\sigma_d$ | $n_i$ | T | T' | R | $n_i'$ | Infra-red | Raman effect |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $A_1$ .. | 1 | 1 | 1 | 1 | 1 | 4 | 0 | 0 | 1 | 3 | .. | P |
| $A_2$ .. | 1 | 1 | 1 | −1 | −1 | 5 | 0 | 0 | 1 | 4 | .. | .. |
| $B_1$ .. | 1 | −1 | 1 | 1 | −1 | 6 | 0 | 2 | 0 | 4 | .. | D |
| $B_2$ .. | 1 | −1 | 1 | −1 | 1 | 7 | 1 | 1 | 0 | 5 | M | D |
| E .. | 2 | 0 | −2 | 0 | 0 | 13 | 1 | 3 | 2 | 7 | M | D |
| $U_R$ .. | 16 | 4 | 4 | 2 | 0 | | | | | | | |
| $U_R(S)$ .. | 4 | 4 | 4 | 0 | 0 | | | | | | | |
| $U_R(s-v)$ .. | 2 | 2 | 2 | 0 | 0 | | | | | | | |

If we neglect the coupling around the two-fold axis, the point group symmetry at the positions of the $H_2PO_4$ ions is only $S_4$ and consequently we should expect only 15 internal frequencies to appear in Raman effect. However, we find experimentally only 10 lines, some of which are broad and show some structure. A study of the Raman spectra of these two phosphates at low temperatures shows no radical change in width. In view of this fact it appears probable that the breadth of some of the lines is not so much of thermal origin, as due to an overlapping of faint and diffuse lines.

TABLE II

| Vibration Type | Frequency shift in $cm.^{-1}$ |
|---|---|
| A | 358, 370, 913 |
| B | 393, 467, 2500, 2700 |
| E | 528, 570, 1080 |

If the fairly large birefringence of the crystal is taken as a measure of the optical anisotropy of the $H_2PO_4$ groups, then the lattice oscillations of the rotatory type will appear with considerable intensity. The frequency

shifts 98 and 114 cm.$^{-1}$ have therefore to be attributed to the rotational oscillations of the $H_2PO_4$ groups, though the observed variation of intensity of the 114 cm.$^{-1}$ line with orientation is in disagreement with what should be expected for the degenerate class (Chapelle, 1949).

The frequencies of the translatory type of oscillations may be evaluated to a first approximation by taking into consideration the forces between the closest neighbours, as has been done in detail for $NH_4H_2PO_4$ by Jean Chapelle. The force constants used are given below along with the co-ordinates of the groups between which they act. $k_1 - (000) - (\frac{1}{2}0\frac{1}{4})$, $k_2 - (000) - (\frac{1}{2}\frac{1}{2}0)$, $k_3 - (000) - (00\frac{1}{2})$, $k_4 - (000) - (0\frac{1}{2}\frac{1}{4})$, $k_5 - (00\frac{1}{2}) - (0\frac{1}{2}\frac{1}{4})$.

The constants $k_2$ and $k_3$ may be evaluated utilising the relations given by Chapelle and the values of the elastic constants reported by Mason (1947).

$C_{66} = 6{\cdot}1 \times 10^{10}$ dynes per cm.$^2$ $C_{44} = 12{\cdot}8 \times 10^{-10}$ dynes per sq. cm.

$S_{33} = 2{\cdot}1 \times 10^{-12}$ cm.$^2$/dyne. $S_{11} = 1{\cdot}7 \times 10^{-12}$ cm.$^2$/dyne.

$S_{12} = -{\cdot}4 \times 10^{-12}$ cm.$^2$/dyne.

Identifying the line 185 cm.$^{-1}$ as belonging to the class E, we evaluate all the other frequencies and force constants (C.G.S.) $k_2 = {\cdot}21 \times 10^4$, $k_3 = 1{\cdot}89 \times 10^4$, $k_4 = 3{\cdot}31 \times 10^4$, $k_1 = 2{\cdot}78 \times 10^4$, $k_5 = -1{\cdot}38 \times 10^4$, while the corresponding values for $NH_4H_2PO_4$ are $k_5 = ({\cdot}22 \pm {\cdot}02) \times 10^4$, $k_3 = {\cdot}82 \times 10^4$, $k_4 = 1{\cdot}52 \times 10^4$, $k_1 = 2{\cdot}3 \times 10^4$, $k_4 = {\cdot}24 \times 10^4$.

Comparing the two we find that one may legitimately expect a close correspondence between the oscillations in the two crystals which are antisymmetric with respect to the four-fold axis and some difference in the case of symmetric oscillations. However, as there are no symmetric oscillations in both these cases, the spectra show a striking similarity in accordance with our expectation.

TABLE III

*External oscillations in $KH_2PO_4$*

| Type | Calculated in cm.$^{-1}$ | Observed in cm.$^{-1}$ |
|---|---|---|
| $B_1$ | 72<br>189 | 50–60<br>185 |
| $B_2$ | 189 | 185 |
| E | 150<br>185<br>230 | 153<br>185<br>.. |

In conclusion, the author wishes to express his gratitude to Professor R. S. Krishnan for his constant encouragement.

## Summary

The Raman spectrum of potassium di-hydrogen phosphate has been studied using the $\lambda$ 2537 radiation of a quartz mercury arc. It consists of 15 lines of which 10 are due to internal osciallations of the $H_2PO_4$ group, 2 rotatory oscillations of the $H_2PO_4$ groups and 3 translatory type of external oscillations. Following Jean Chapelle, an approximate calculation of the frequencies of translatory type of oscillations has been made and compared with those observed.

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# THERMAL EXPANSION OF CRYSTALS

## Part VI. Alumina

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### 1. Introduction

Corundum or alumina, $Al_2O_3$, has been known as a naturally occurring mineral since long and it is reputed for its hardness, being next only to diamond. Many of its physical properties have been investigated extensively. Amongst various others, the Raman effect of this crystal has been thoroughly investigated by R. S. Krishnan (1947). Deutschbein (1932, 33, 34), Venkateswaran (1935) and Anna Mani (1942) investigated the luminescence properties of alumina containing chromic oxide as an impurity. Recently the elastic constants of this substance have been determined by Rao (1949) in this laboratory. However, the thermal expansion data of this crystal are very meagre and incomplete. Fizeau (1865) was the first to determine the coefficient of thermal expansion of the natural mineral at 40° C. Due to the importance of alumina as a refractory material for industrial applications, its thermal behaviour has been studied by some workers. Thus, Halmang and Gaeris (1935); Ebert and Tingwaldt (1936) have studied the linear dilatation of corundum upto 1600° C., while Hindl (1933) studied the same for synthetic variety containing 95% of $Al_2O_3$. Although the results of these investigators are valuable in their own way, they do not elucidate the very important anisotropic expansion of the crystal along and perpendicular to the principal trigonal axis. X-ray measurements of lattice parameters extending over a wide range of temperatures are reported in the literature (Büssen, Blüth and Grochtmann, 1935), but unfortunately the author could not have access to the journal. The present paper describes the results of the interferometric study of thermal expansion of this crystal along the two crystallographic axes.

### 2. Procedure of the Experiment

Naturally occurring corundum being unavailable, synthetic alumina was used in the present investigation. The specimen was in the form of approximately a semi cylindrical boule made up of a single crystal of corundum.

The determination of the optic axis was effected by means of a pair of ordinary polaroids. The optic axis was found to lie in the plane surface of the semi cylinder, inclined at an angle to the lengthwise axis of the boule. The sections parallel and perpendicular to the optic axis were cut by carefully fixing the specimen by gadgets on a cutting machine. The sections were then converted as usual into right pyramids with their altitudes in the desired orientation.

## 3. Results

The coefficients of thermal expansion along and perpendicular to the optic axis are entered in Tables I and II respectively. The values calculated from the interpolation formula, inserted at the top of the table, are also entered for comparison. The difference, in percentage, between the experimental and interpolated values has been inserted in the last column of each table. The variation of the coefficients of linear expansion is depicted graphically in Fig. 1. Unfortunately due to the difficulty of cutting and grinding the spacers, no determination was made along any other arbitrarily cut direction for the purpose of verification of the above experimental values.

### Table I

*Coefficient of linear expansion of alumina parallel to the optic axis*

$$\alpha_{\parallel} = 0{\cdot}0_5 6582 + 0{\cdot}0_8 4995\, t + 0{\cdot}0_{11} 2578\, t^2$$

| Temperature (° C.) | $\alpha \times 10^6$ (Observed) | $\alpha \times 10^6$ (Calculated) | Difference (%) |
|---|---|---|---|
| 51·7 | 6·85 | 6·85 | .. |
| 94·7 | 7·05 | 7·08 | −0·4 |
| 135·3 | 7·36 | 7·30 | +0·5 |
| 173·9 | 7·53 | 7·53 | .. |
| 210·2 | 7·72 | 7·74 | −0·3 |
| 250·7 | 7·95 | 8·00 | −0·6 |
| 293·9 | 8·31 | 8·27 | +0·5 |
| 335·2 | 8·60 | 8·54 | +0·7 |
| 375·0 | 8·85 | 8·82 | +0·3 |
| 417·4 | 9·11 | 9·11 | .. |
| 462·1 | 9·46 | 9·44 | +0·2 |
| 505·3 | 9·73 | 9·76 | −0·3 |
| 547·1 | 10·02 | 10·08 | −0·6 |
| 587·6 | 10·36 | 10·40 | −0·4 |
| 629·9 | 10·73 | 10·75 | −0·2 |
| 676·9 | 11·15 | 10·14 | .. |

TABLE II

*Coefficient of linear expansion of alumina perpendicular to the optic axis*

$\alpha_{\perp} = 0{\cdot}0_5 5425 + 0{\cdot}0_8 5534\, t + 0{\cdot}0_{11} 2876\, t^2$

| Temperature (°C.) | $\alpha \times 10^6$ (Observed) | $\alpha \times 10^6$ (Calculated) | Difference (%) |
|---|---|---|---|
| 53·6 | 5·72 | 5·73 | .. |
| 95·6 | 5·98 | 5·98 | .. |
| 134·8 | 6·24 | 6·22 | +0·3 |
| 171·7 | 6·46 | 6·46 | .. |
| 207·1 | 6·65 | 6·69 | −0·6 |
| 245·2 | 6·90 | 6·95 | −0·7 |
| 285·6 | 7·23 | 7·24 | .. |
| 324·0 | 7·51 | 7·52 | .. |
| 360·7 | 7·86 | 7·79 | +0·9 |
| 399·6 | 8·04 | 8·10 | −0·8 |
| 440·6 | 8·39 | 8·42 | −0·4 |
| 479·6 | 8·71 | 8·74 | +0·4 |
| 517·3 | 9·01 | 9·06 | −0·6 |
| 553·7 | 9·32 | 9·37 | −0·6 |
| 594·5 | 9·73 | 9·73 | .. |
| 639·2 | 10·16 | 10·14 | +0·2 |
| 684·4 | 10·65 | 10·56 | +0·9 |

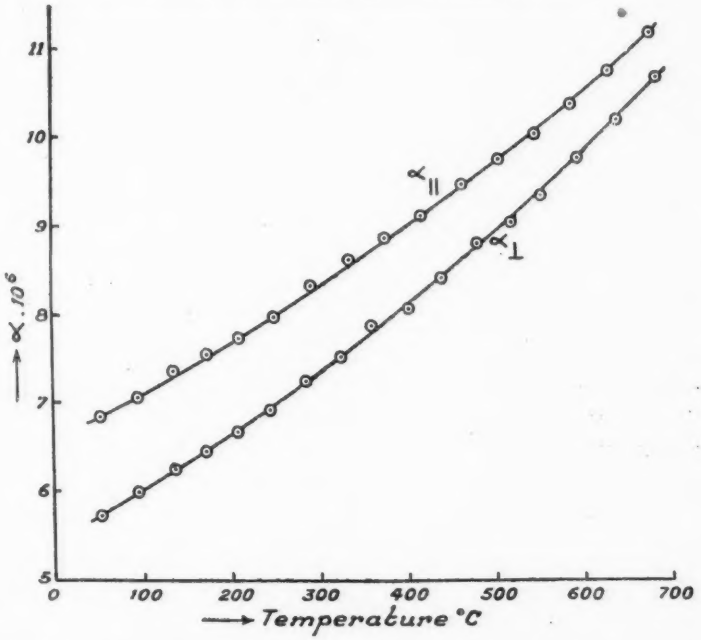


FIG. 1. Variation of coefficients of expansion of alumina with temperature

## 4. Discussion

From the results given above, it is readily seen that at room temperature the values of the coefficients of thermal expansion of alumina along the crystallographic axes are sufficiently low. This crystal has been shown to possess comparatively very high elastic constants. These facts are in qualitative conformity with the fact that the substance is the hardest next to diamond. Moreover, it is found that the anisotropy in thermal expansion is also very small. Thus the lattice is of the isosthenic type in which the atoms or ions are linked to all their neighbours with bonds of the same strength. The elastic behaviour of alumina should, therefore, exhibit inappreciable difference in the values of the elastic constants parallel and perpendicular to the optic axis. This is confirmed by the experimental results of Rao (1949), according to whom $S_{11} = 2{\cdot}84 \times 10^{-13}$cm.$^2$/dyne and $S_{33} = 2{\cdot}21 \times 10^{-13}$ cm.$^2$/dyne. A similar behaviour was observed by the author (Sharma, 1950) in the case of hæmatite, for which the thermal anisotropy was found to be vanishingly small at the room temperature and the elastic modulii practically equal.

X-Ray studies on the crystal structure of alumina and hæmatite by Bragg and Bragg (1919) and by Pauling and Hendricks (1925) reveal that the crystal structures of these two substances are very nearly identical. Even the rhombohedral angle for both the lattices is the same, *i.e.*, equal to 55° 17′. Thus the lattice is not very much different from the face-centred cubic lattice, for which the corresponding angle is 54° 44′. Hence the thermal expansion of the rhombohedral lattice of these crystals exhibits so little an anisotropy at the room temperature.

However, a closer scrutiny of the thermal behaviour of these two crystals exhibits a very peculiar difference. For the sake of comparison, the data for the coefficients of expansion at different temperatures are entered in Table III.

Table III

*Comparative study of the thermal expansion of $Al_2O_3$ and $Fe_2O_3$*

| Temperature | | 0°C. | 100°C. | 200°C. | 300°C. | 400°C. | 500°C. | 600°C. | 700°C. | Elastic modulus |
|---|---|---|---|---|---|---|---|---|---|---|
| $\alpha_{11} \times 10^6$ | $Al_2O_3$ | 6·58 | 7·11 | 7·68 | 8·31 | 8·99 | 9·72 | 10·51 | 11·34 | $2{\cdot}84 \times 10^{-13}$ |
| | $Fe_2O_3$ | 7·90 | 8·50 | 9·25 | 10·14 | 11·18 | .. | .. | .. | $4{\cdot}41 \times 10^{-13}$ |
| $\alpha_{11} \times 10^6$ | $Al_2O_3$ | 5·42 | 6·01 | 6·45 | 7·34 | 8·10 | 8·91 | 9·78 | 10·71 | $2{\cdot}21 \times 10^{-13}$ |
| | $Fe_2O_3$ | 7·83 | 9·00 | 10·40 | 12·03 | 13·90 | .. | .. | .. | $4{\cdot}43 \times 10^{-13}$ |

From the above Table it is clear that while for alumina $\alpha_{11} > \alpha_1$, the inequality is reversed in the case of hæmatite. Similar behaviour is exhibited by their respective elastic moduli. It may therefore be concluded that the anisotropy of thermal expansion of a uniaxial crystal is in the same sense and of the same order of magnitude as the anisotropy of the principal elastic modulus. As the crystal is heated above the room temperature, the thermal anisotropy in the case of alumina diminishes, though slowly, while in the case of hæmatite it rapidly goes on increasing with temperature. The trends of the curves reproduced in this paper and the author's previous publication on hæmatite bring out this fact more vividly. Moreover, in the case of hæmatite it was found that the crystal behaved like an isotropic substance at 12° C., below which the sign of the anisotropy was reversed. No such peculiarity is observed in the case of alumina in whose case the thermal anisotropy seems to vanish at very high temperatures, as the interpolation formulæ for the two directions indicate. In view of the identity of the two lattices, it is very difficult to adduce any plausible explanation for this peculiar difference in their thermal behaviour.

The author takes this opportunity to express his gratitude to Professor R. S. Krishnan for his constant guidance and keen interest in the work.

## 5. Summary

The paper describes the results of interferometric study of thermal expansion of alumina along and perpendicular to the optic axis. The principal coefficients of expansion are given by

$$\alpha_{11} = 0{\cdot}0_5 6582 + 0{\cdot}0_8 4995\, t + 0{\cdot}0_{11} 2578\, t^2.$$

$$\alpha_{\perp} = 0{\cdot}0_5 5425 + 0{\cdot}0_8 5534\, t + 0{\cdot}0_{11} 2876\, t^2.$$

It is found that the anisotropy in thermal expansion is closely related to the anisotropy in the principal elastic modulus.

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